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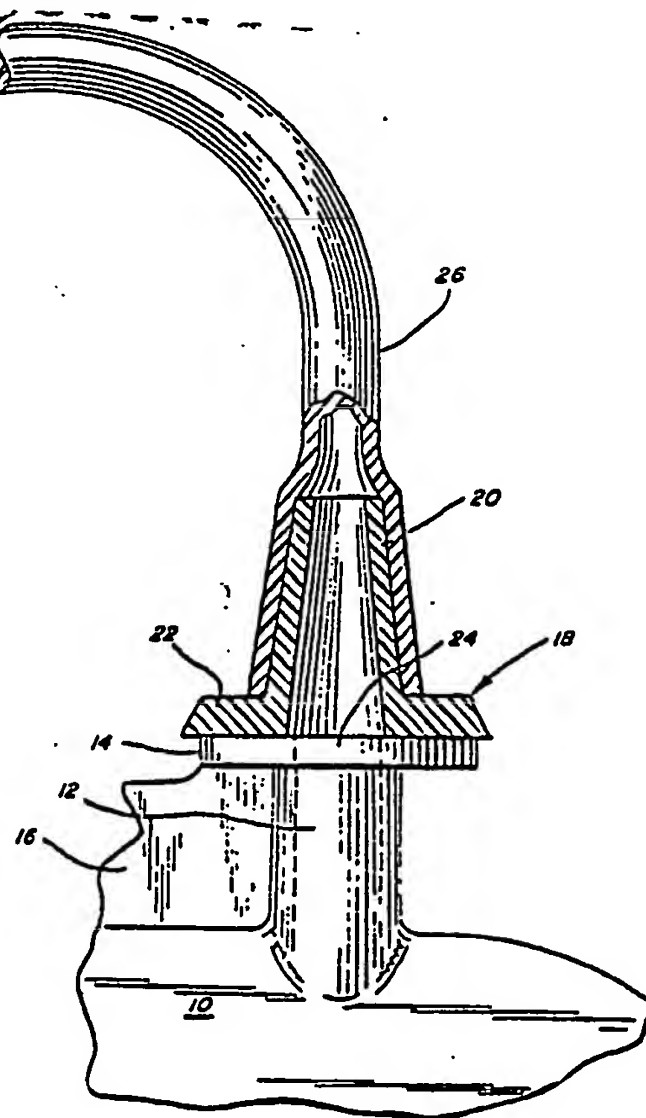
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(54) Title: CONNECTION OF POLYVINYL CHLORIDE TO ESSENTIALLY POLYOLEFIN MATERIALS

(57) Abstract

A connector (18) capable of simultaneous sealing with improved strength to both polyvinyl chloride plastics and essentially polyolefin plastics. The formulation comprises certain block copolymers admixed with a small amount of polypropylene and optionally (ethylene-vinyl acetate).



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CONNECTION OF POLYVINYL CHLORIDE TO
ESSENTIALLY POLYOLEFIN MATERIALS

Technical Field and Description of Prior Art

In the copending U.S. Patent Application Serial No. 5 067,068, filed August 15, 1979, now U.S. Patent No. 4,327,726, by Peter C. Kwong and Dean G. Laurin, a connector member for dissimilar materials is disclosed. Specifically, the connector member is made out of a plastic formulation which is adherent both to polyvinyl chloride and to certain materials which are substantially of polyolefin nature. The connector may be heat sealed to the polyolefin-type material, while it is solvent-bonded to the polyvinyl chloride. Thus, for example, a blood bag made of a modified polyolefin-type material containing 15 polypropylene, a block copolymer of polystyrene blocks and rubber polyolefin blocks, and poly(ethylene-vinyl acetate) may be bonded through such a connector to a polyvinyl chloride donor tube, where normally there is virtually no adhesion at all between those two materials.

20 Specifically, the material of the connector of the above-cited application is a mixture which comprises 65 percent of a blend of 20 parts by weight of a polypropylene-based material, 60 parts by weight of a polystyrene-poly(ethylene-butylene) block copolymer, and 25 20 parts by weight of poly(ethylene-vinyl acetate); and 35 percent of a polyester type block copolymer.

However, while such a material is solvent-bondable to polyvinyl chloride, it is not as strongly adherent to the polyvinyl chloride as might be desired in numerous circumstances, since the bonded joint between the two materials 30 can be separated with a relatively low force.

In Hoh et al. U.S. Patent No. 3,832,314 a segmented copolyester adhesive and coating composition is disclosed



in which a thermoplastic, segmented copolyester elastomer is mixed with a low molecular weight thermoplastic resin such as a styrene polymer, a chlorinated aliphatic hydrocarbon wax or the like. Such a structure, however, is not contemplated for the use of this invention, and does not include polystyrene-rubbery olefin block copolymer contemplated for use in this invention.

In accordance with this invention, an improvement in the formulation disclosed in the above-cited patent application is provided, resulting in a plastic composition and a connector member made of such composition which is capable of simultaneous, stronger sealing to both polyvinyl chloride plastics and essentially polyolefin plastics ranging from polypropylene to the modified polyolefin plastic formulation described above containing the polypropylene, the polystyrene-rubbery polyolefin block copolymer, and the poly(ethylene-vinyl acetate).

Description of the Invention

In accordance with this invention, a plastic composition is provided which is capable of simultaneously sealing to both polyvinyl chloride plastics and essentially polyolefin plastics. The formulation comprises:

- (a) from 1 to 8 percent by weight of a polyolefin consisting essentially of propylene units;
- 25 (b) from 40 to 65 percent by weight of a block copolymer, having thermoplastic rubber characteristics, consisting essentially of blocks, preferably comprising 50 to 85 percent by weight of the polymer molecule, of a rubbery olefin polymer, and blocks of polystyrene;
- 30 (c) from 35 to 55 percent by weight of a flexible block copolymer of covalently-bonded polybutylene terephthalate units and poly(1,4-butylene oxide) units; and



(d) from 0 to 15 percent by weight of a poly(ethylene-vinyl acetate) softening agent containing preferably no more than 35 percent by weight of vinyl acetate units.

The plastic composition of this invention can be heat sealed to polypropylene, polyethylene, and other true polyolefin materials. Also, it can be heat-sealed to modified polyolefin-type blends for making flexible, collapsible containers and other items as described above and as disclosed in U.S. Patent No. 4,140,162.

On the other hand, as stated above, the connector and formulation of this invention adheres very well, by solvent sealing using methylisobutylketone or acetone for example, to polyvinyl chloride formulations so that the polyvinyl chloride component of a device, for example donor tubing, may be reliably and firmly sealed to a blood bag made of one of the above described polyolefin-type formulations. In the absence of the connector of this invention, polyvinyl chloride simply does not seal at all to most substantially polyolefin formulations.

The term "polyolefin" as used herein is intended to denote halogen-free materials which are polymerized by the basic vinylic polymerization reaction of ethylene or a substituted ethylene. It is contemplated that certain amounts of substituted ethylene materials may be present, such as styrene, acrylonitrile vinyl acetate, and the like, which cause the material to be not true polyolefins. These are still contemplated to be within the scope of this invention as essentially polyolefin materials, since their polymerization still approximates the vinylic polymerization reaction of ethylene, and related olefins such as propylene and butadiene.

Basically, the formulation of this invention differs from the formulation of the previously cited patent application in that the polypropylene ingredient (a) is reduced



in quantity. Surprisingly, this turns out to greatly improve the capability of the formulation to be solvent bonded to polyvinyl chloride, while still providing excellent heat seal adhesion to many polyolefin-type formulations such as those described above. However, the presence of at least 1 percent and preferably 1.5 to 6 percent of polypropylene, or a material consisting essentially of polypropylene units with only minor amounts of added units such as ethylene, is desirable for improved heat sealing to many of the polyolefin-type materials.

Ingredient (b), the block copolymer of styrene and the rubbery olefin, preferably is a block copolymer of polystyrene with poly(ethylene-butylene), with the ethylene and butylene being in approximately equal quantities. Such materials are sold by the Shell Chemical Company under trademark Kraton G. Alternatively, similar materials sold by the Shell Chemical Company include block copolymers of styrene and polybutadiene.

Ingredient (c) of the plastic composition of this invention may be a flexible block copolymer of covalently bonded polybutylene terephthalate and poly(1,4-butylene) oxide units. Preferably the butylene oxide (polyether) blocks comprise from 50 to 70 percent by weight of the flexible block copolymer composition, for example 60 percent. A type of block copolymer is available from E. I. DuPont deNemours & Company under the trade name HYTREL. The specific material sold under the trade name HYTREL 4056 is preferred for use herein. Preferably, the flexible block copolymer of ingredient (c) may exhibit a melt flow rate of no less than 15 and typically 18 grams per 10 minutes at 220° C. as described in the test of ASTM D1238. Of course, the material of ingredient (c) should have sufficient molecular weight to be a solid thermoplastic material of satisfactory structural integrity.



Ingredient (d), the poly(ethylene-vinyl acetate), may also be added as desired to lubricate the flow of the material of the connector of this invention during heat seal. Also, it may be a lower cost material than ingredient (c), which it may partially, but not completely, replace in accordance with this invention.

Frequently, the blended material made from ingredients (a) through (d) is white, rather than being translucent or transparent, implying a certain amount of phase incompatibility. Nevertheless, highly satisfactory connector parts may be made from the material, and its tensile and other physical properties and softening temperature may be sufficient for autoclaving and other normal handling of disposable medical devices with which it may be used.

Pellets of the ingredients of the plastic composition of this invention may be simply mixed together in their proper ratio and poured into an injection molding machine. The molding screw takes care of the final mixing in the melted state, so that the formulation of the material can take place simultaneously with the molding process.

The polyolefin ingredient (a) is substantially polypropylene, but may contain for example from 2 to 5 percent by weight of ethylene units or the like. A small amount of at least about 1.5 percent by weight of the polyolefin ingredient (a) is preferred to improve the heat sealing characteristics of the material, while the solvent bonding capability of the formulation to polyvinyl chloride begins to be reduced at concentrations of ingredient (a) above 6 percent, although it remains improved up through at least about 8 percent by weight of ingredient (a).

EXAMPLE I

A formulation of this invention was mixed in an injection molding machine, containing (a) 2 percent by weight



of polypropylene having a minor amount of ethylene units; (b) 50 percent by weight of Kraton G 1660 poly(styrene-ethylene butylene) block copolymer; (c) 38 percent of HYTREL 4056 polyester block copolymer; and (d) 10 percent. 5 by weight of poly(ethylene-vinyl acetate) containing about 28 percent of vinyl acetate units. Such a blended material may be extruded into strips, or formed into a connector in accordance with this invention.

As a specific demonstration of its bonding strength to 10 polyvinyl chloride, thin strips of the above formulation were solvent-bonded with cyclohexanone to a strip of a polyvinyl chloride formulation plasticized with di-2-ethylhexylphthalate. The surfaces of both strips were wetted by cyclohexanone. The wetted sides were joined 15 together and held under pressure overnight for drying.

For testing, an unbonded end of each of the sample strips were clamped to the jaws of an Instron testing machine. The cross head speed of the test was 10 inches per minute; the chart speed 10 inches per minute; and the 20 full scale was 10 pounds. The force required to tear the two strips apart was 5.97 pounds per inch.

This exceeds by about 40-fold the comparable results obtained when the specifically-disclosed formulation of the previously cited patent application is similarly 25 tested, that material requiring approximately 0.14 pound per inch for separation from the same type of polyvinyl chloride strip.

EXAMPLE II

The following formulation was blended into a homo- 30 geneous material: (a) 5 percent by weight of the same polypropylene formulation as in Example I; (b) 45 percent by weight of the poly(styrene-ethylene butylene) block copolymer of Example I; and (c) 50 percent by weight of the polyester type block copolymer of Example I. This



formulation was formed into strips and tested by bonding to the same polyvinyl chloride formulation as in Example I. 5.05 pounds per inch were required to pull the two strips apart.

5 In the drawing, Figure 1 is a fragmentary, elevation view, taken partly in vertical section, of a blood bag of a generally known design, made of an essentially polyolefin blend, carrying the connector of this invention, which, in turn, is connected to donor tubing made of a
10 polyvinyl chloride formulation.

Referring to the drawing, blood bag 10 is shown, which may be of conventional design. Blood bag 10 may be made of a polyolefin blend which may include 20 parts by weight of a polypropylene polymer having a melt flow of about 2,
15 with a small amount of copolymerized ethylene; 60 parts by weight of a block copolymer having thermoplastic rubber characteristics, consisting of a central block of poly(ethylene-butylene) and terminal blocks of poly-
20 acetate) copolymer.

Blood bag 10 as shown defines an access port 12 which in turn defines a terminal flange 14 which is integrally formed in relatively thick section along with the thinner sections of the flexible walls of blood bag 10. Web 16 as
25 shown communicates between port 12 of the blood bag and an adjacent port (not shown). In accordance with this invention, connector member 18 is disclosed, being preferably an injection molded, single piece of the formula of this invention, comprising a tubular portion 20 and
30 terminating in a flange 22. Connector member 18 may be of the formulation described in Example I above.

Flange 22 of connector 18 may be conventionally heat sealed to flange 14 of the blood bag, using for example an ultrasonic sealing device or a spin welding device, so



that a common bore 24 passes between connector 18 and port 12 of the blood bag.

Additionally, polyvinyl chloride donor tubing 26 may be solvent-sealed to the exterior of tubular portion 20 of connector 18, using, for example, cyclohexanone or any other appropriate volatile solvent for both of the materials. Both flange 14 and tubing 26 adhere strongly to connector 18 with the result that great simplification of the bond between these dissimilar materials may be obtained.

The above has been offered for illustrative purposes only, and is not intended to limit the invention of this application, which is as defined in the claims below.



THAT WHICH IS CLAIMED IS:

1. A plastic composition which is capable of simultaneously sealing to both polyvinyl chloride plastics and essentially polyolefin plastics, which comprises:

5 (a) from 1 to 8 percent by weight of a polyolefin consisting essentially of propylene units;

(b) from 40 to 65 percent by weight of a block copolymer, having thermoplastic rubber characteristics, consisting essentially of blocks of rubbery olefin polymer and
10 blocks of polystyrene;

(c) from 35 to 55 percent by weight of a flexible block copolymer of covalently bonded polybutylene terephthalate units and poly(1,4-butylene oxide) units; and

(d) from 0 to 15 percent by weight of poly(ethylene-
15 vinyl acetate.

2. The composition of Claim 1 in which from 1.5 to 6 percent by weight of said polyolefin consisting essentially of propylene units is present.

3. The composition of Claim 1 in which said composition contains essentially 2 percent of ingredient (a); 50
20 percent of ingredient (b); 38 percent of ingredient (c); and 10 percent of ingredient (d).

4. The composition of Claim 1 in which the rubbery olefin polymer is poly(ethylene-butylene).

25 5. The plastic composition of Claim 1 in which said block copolymer of ingredient (c) contains from 50 to 70 percent by weight of said poly(1,4-butylene oxide) blocks.



6. A plastic composition which is capable of simultaneously sealing to both polyvinyl chloride plastics and essentially polyolefin plastics, which comprises:

(a) 1.5 to 6 percent by weight of a polyolefin
5 consisting essentially of propylene units;

(b) from 45 to 55 percent of a block copolymer having thermoplastic rubber characteristics, consisting essentially of (1) a central block of poly(ethylene-butylene) comprising 50 to 85 percent by weight of the polymer and
10 having rubbery characteristics and (2) terminal blocks of polystyrene;

(c) from 40 to 55 percent by weight of a flexible block copolymer of covalently bonded polybutylene terephthalate units and poly(1,4-butylene oxide) units; and

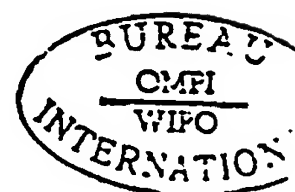
15 (d) from 5 to 15 percent of poly(ethylene-vinyl acetate) containing no more than 35 percent by weight of vinyl acetate units.

7. The plastic composition of Claim 6 in which said block copolymer of ingredient (c) contains from 50 to 70
20 percent by weight of said poly(1,4-butylene oxide) blocks.

8. A connector which is capable of simultaneously sealing to both polyvinyl chloride plastics and essentially polyolefin plastics, said connector being made of a material which comprises:

25 (a) from 1 to 8 percent by weight of a polyolefin consisting essentially of propylene units;

(b) from 40 to 65 percent by weight of a block copolymer, having thermoplastic rubber characteristics, consisting essentially of (1) a central block comprising
30 50 to 85 percent by weight of a rubbery olefin polymer and (2) terminal blocks of polystyrene;



(c) from 35 to 55 percent by weight of a flexible block copolymer of covalently bonded polybutylene terephthalate units and poly(1,4-butylene oxide) units; and

(d) from 0 to 15 percent by weight of poly(ethylene-5 vinyl acetate).

9. The connector of Claim 9 in which from 1.5 to 6 percent by weight of said polyolefin consisting essentially of propylene units is present.

10. The connector of Claim 9 in which said composition contains essentially 2 percent of ingredient (a); 50 percent of ingredient (b); 38 percent of ingredient (c) and 10 percent of ingredient (d).

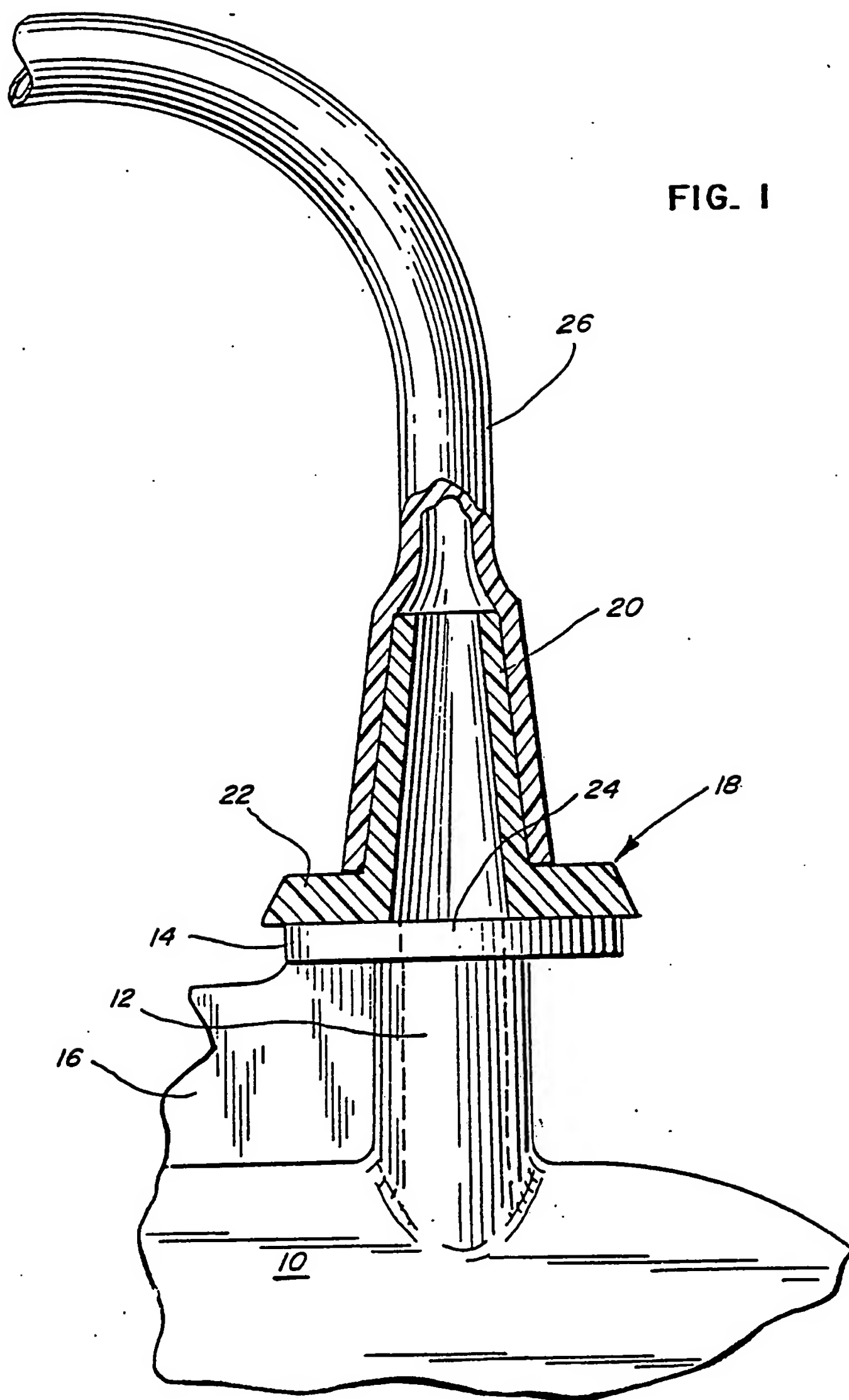
11. The connector of Claim 9 in which the rubbery olefin polymer is poly(ethylene-butylene).

12. The plastic composition of Claim 1 in which said block copolymer of ingredient (c) contains from 50 to 60 percent by weight of said poly(1,4-butylene oxide) blocks.

13. The connector of Claim 8 in which from 2 to 5 percent of ingredient (a), from 45 to 55 percent of ingredient (b), from 45 to 55 percent of ingredient (c), and from 5 to 15 percent of ingredient (d) are present, and said poly(ethylene-vinyl acetate) contains no more than 35 percent by weight of vinyl acetate units.



FIG. 1



INTERNATIONAL SEARCH REPORT

International Application No PCT/US82/01028

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ³		
According to International Patent Classification (IPC) or to both National Classification and IPC INT. CL. 3 C08L 53/00, 53/02, 67/02; B32B5/22 US CL. 525/89, 92		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁴		
Classification System	Classification Symbols	
U.S.	525/89, 92 ;	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁵		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴		
Category ⁶	Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸
X,P	US, A, 4,327,726, PUBLISHED 04 MAY 1982 Kwong et al Col. 2, lines 26-68	1-13
Y	US, A, 4,090,996, PUBLISHED 23 MAY 1978 GERGEN ET AL	1-13
Y	US, A, 4,011,286, PUBLISHED 08 MARCH 1977 SEYMOUR ET AL	1-13
Y	US, A, 3,865,776, PUBLISHED 11 FEBRUARY 1975 GERGEN	1-13
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IV. CERTIFICATION		
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